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ABSTRACT

First responders, radiation detection specialists, and nuclear operators need simple, rapid, and reliable field equipment to detect radionuclide contamination. When responding to an event, hand-held detectors may provide adequate screening for beta/gamma/neutron-emitting radionuclides but lack the field sensitivity and adaptability for alpha-emitting radiological species like uranium (U) and plutonium (Pu). A new selective colorimetric technology has been developed for response personnel to characterize contamination from actinides, such as U and Pu, for both field contamination events and everyday maintenance testing at nuclear facilities. Experimentation has provided both selectivity and sensitivity for U and Pu in several rapid chemical techniques. Proof of concept (POC) work, funded through the LDRD Seed program, has shown success with the first of multiple colorimetric agents identified for uranium at parts-per-billion (ppb) levels. Continuing research beyond POC is being performed on a multitude of new areas associated with this technology including: environmental interfering ions (iron, nickel, calcium, potassium, etc.), addition of new actinides of interest that would expand detection capabilities, colorimetric agents and combinations of agents not tested during POC, and new small-scale rapid column separation capabilities for field detection. This work has currently focused on iron as an important interfering ion, and results have shown that iron and other common environmental interferences do not affect the color change with respect to the actinides of interest. Ultimately, additional fundamental research could advance these integrated techniques into a field detection system, improve measurement performance, and broaden the range of detectable radionuclides. This novel chemical detection method will allow civilian and military first responders to more effectively assess a radiological event's magnitude, dimensions, and severity early, thereby helping on-scene coordinators to make crucial decisions quickly. For the nuclear energy and space industry, this proposed work could provide a simple screening test for detection of low-level spills and leaks for nuclear reactor facilities and radioisotope thermal generators (RTG) for space missions.

SIGNIFICANCE

Whether from a radiological dispersal device (RDD), improvised nuclear device (IND), reactor accident, or radiological spill, it is widely recognized that preparing for a major nuclear incident is not about *if* it will happen, but *when*¹. Even in the best of circumstances, most municipalities would face severe challenges in providing effective incident response to a large-scale radiation release caused by nuclear terrorism or nuclear accident. The effectiveness of first responders (the local municipality's law enforcement and fire personnel) and the military to a radiological emergency is hampered by an insufficient amount of nuclide-specific radiation detection equipment. Experience shows that first responders and the military will bear the major burden of coping with nuclear incident response within the context of determining the range of dispersal, inner cordoned area to be secured for investigation, and public protection^{2,3}. Currently, first responders use basic hazard class kits to analyze for unknown materials. These event response

kits are limited and very basic; they are not designed to identify specific substances, especially radionuclides⁴. Much of the contamination from U and Pu species is alpha contamination, which is very difficult to detect with conventional radiological detection methods, due to shielding effects from environmental factors like dust. The industry standard of using radiometric grab-samples for actinides is limited at best, since sampled material requires days of radiochemical separations in a laboratory setting. This is a great disadvantage compared to a rapid onsite chemical detection kit. A rapid chemical detection method would greatly advance the state of the art for the detection of actinides of interest in a radiological event arena. There are currently no onsite chemical analysis methods in use by first responders that provide them protection and aid nuclear forensics investigators. Companies such as Laurus Systems and Canberra Industries provide only portable radiation detection devices, which have limited success with alpha emitters. Using a colorimetric approach to actinide detection allows for substantial time and cost savings over current methods, is easily deployable in the field, is simple to use, and is novel with no known industrial equivalent. A rapid chemical detection method such as this could also be of significance use in the nuclear industry for both maintenance checks at reactor sites and for non-proliferation investigations. At detection levels of ppb, a potential hazard may be identified before becoming a serious problem.

EXPERIMENTAL

POC work showed positive results for U and Pu; however, it also posed new questions and identified fundamental radiochemistry areas that would be beneficial to develop within this research for application in areas of space travel and future space colonization that would employ nuclear power for electrical generation. Indicators (colorimetric agents with structures shown in Appendix 1, Figure 1) such as 1-(2-pyridylazo)-2-naphthol (PAN)⁴ have been used in combination with 2-(5-bromo-2-pyridylazo)-5,5-diethylaminophenol (Br-PADAP)⁵ to increase the intensity of visual color change and selectivity of the actinide of interest. The chemical detection methods tested in the POC showed positive results for use as a rapid colorimetric detection method technology for first responders and all nuclear-related facility and space exploration operations. Research area results included simple separation stages, use of a sprayed colorimetric agent, and a colorimetric agent wet wipe (similar to individually packaged sanitizer wipes). These are used to produce a color change in the presence of actinides such as uranium, plutonium, and potentially thorium. The separation stages can include a filter/leach/rinse process to remove large particles or leach potential contamination from larger debris; a dissolution stage (if needed) to solubilize smaller organic/inorganic material; and use of a polymer gel for solid surfaces such as rock, metal, concrete, asphalt, etc., which can be removed from the surfaces. Current work has produced visual color change at 23.8 ppb U using a 1×10^{-5} M Br-PADAP: PAN and approximately 100 ppm Pu detection with this solution as shown in Appendix 1, Figure 2. Analysis of select environmental interferences, such as iron (Fe), showed no change in color detection, and no precipitate was formed as seen in other colorimetric agents tested with Fe (Figure 1, d). Other colorimetric compounds, as well as rapid detection methods, have been tested. These include: a simple syringe separation method as shown in Appendix 1, Figure 3(a), with two or three separate chambers containing extraction resins for the target analyte (such as Eichrome TEVA[®] and U-TEVA[®] resins for Pu and U, respectively); masking agents (such as ethylenediaminetetraacetic acid [EDTA], diethylenetriaminepentaacetic acid [DTPA], and sodium citrate used to remove interfering species such as iron, copper, lead, and other metals); or

pH adjustment to mitigate false positive/negative responses. The colorimetric indicators were also tested for use in rapid, easy-to-use methods, such as colorimetric spray agents, and a colorimetric permeated towel/wipe as shown in Figure 3(b,c). Such methods can be used for spot checks on nuclear equipment, including those used in propulsion, as well as on surfaces and loose material during a first response to a radiological event (e.g., gravel, stones, and organic material including plant matter). Of the five non-hazardous, environmentally friendly colorimetric agents, both the Br-PADAP and PAN showed the greatest affinity for U and Pu compound formation. Ultraviolet visible spectra of varied concentrations of U in water contacted with 1×10^{-5} M Br-PADAP: PAN 2:1 ratio as shown in Appendix 1, Figure 4. Ultraviolet visible spectra of U using a combination of Br-PADAP: PAN in a 2:1 ratio indicated a significantly higher absorbance over Br-PADA and NaF alone. The visual color using this combination in a 2:1 ratio Br-PADAP: PAN was significantly enhanced with Br-PADA alone, which gave an absorbance no higher than 0.005 nm in previous experimental work. Another important discovery was the Br-PADA: PAN compound did not need a counter anion for stability, unlike the Br-PADA alone, which required NaF incorporation in order to achieve visible color and stabilize the U complex. Ultraviolet visible spectra of the CoDeAc solution (Br-PADAP: PAN compound at a 2:1 ration with $1 \text{E}-5$ M concentration) with varied concentrations of U showed absorbance peaks indicative of U at 578 nm, as shown in Figure 5. Figure 6 shows the absorbance of Idaho Falls drinking water with and without a U tracer using $1 \text{E}-4$ – $1 \text{E}-5$ M Br-PADAP: PAN solution. The spectra show no interference with Fe in this drinking water sample, and the visible color change shows enhancement possible due to the Fe or another mineral present (Figure 7). This technology is currently at Technology Readiness Level (TRL) 4 and can easily achieve TRL 5 and 6 over the next two years at the current rate of development.

This new technology will allow multiple radiation and nuclear agencies to evaluate a contamination, immediately giving them the ability to set up safety zones, pinpoint contamination, collect far fewer samples, and set up decontamination areas using real-time data instead of assumptions. This will better protect the public, as well as first responders, in minutes instead of days or weeks of waiting for laboratory results. This technology will also impact the safety and maintenance of nuclear facilities. It will provide the ability to identify potential leaks in key assemblies with a simple wipe or spray of an agent that turns color in the presence of determinant actinides. The significance of this proposed work could be invaluable to both National and Homeland Security (NHS) and International Safeguards, as well as the general nuclear energy arena and NASA.

References

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Appendix 1.

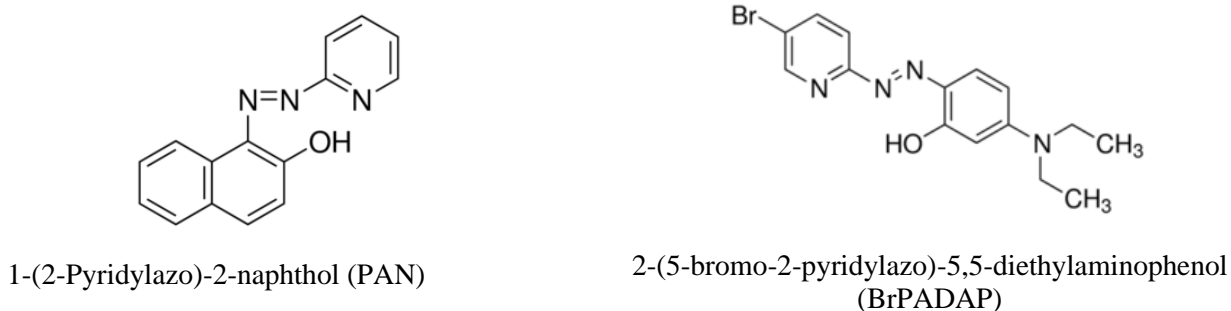


Figure 1. Br-PADAP and PAN structures.

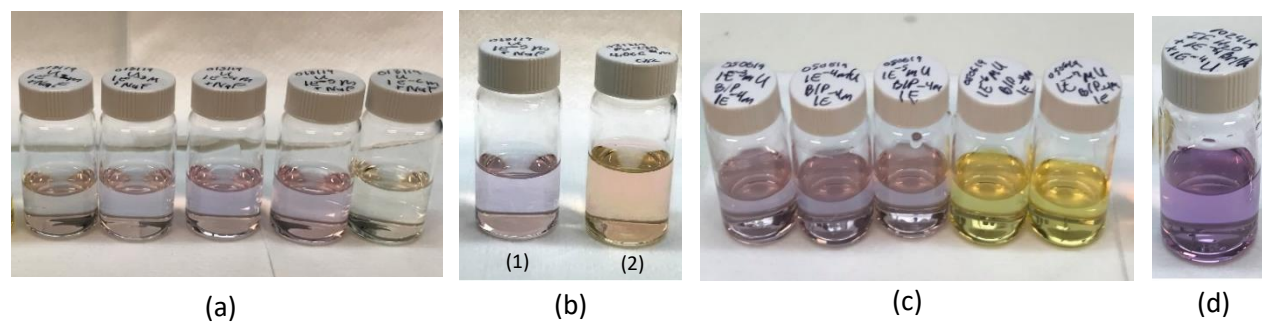
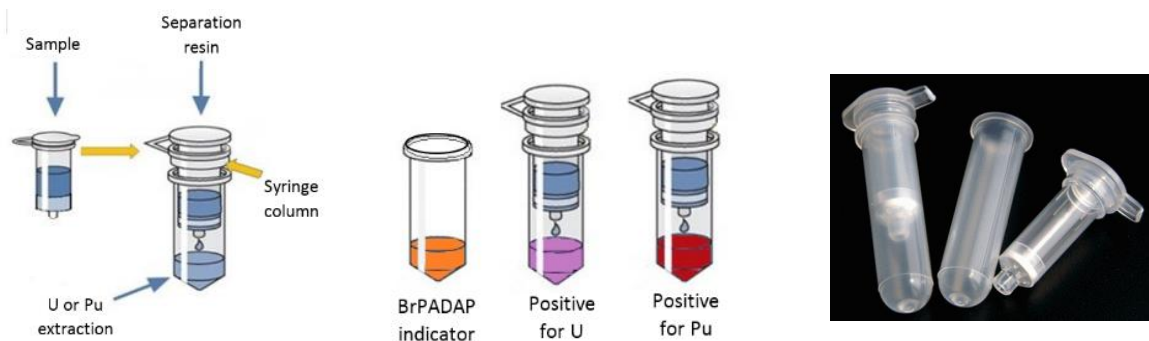


Figure 2. (a): 1×10^{-5} M Br-PADAP indicator contacted with 1×10^{-2} M – 1×10^{-6} M U (from $\text{UO}_2(\text{NO}_3)_2$ in H_2O). A counter anion (NaF) was needed to stabilize the U complex in solution. (b): 1×10^{-5} M Br-PADAP indicator contacted with 1×10^{-5} M U turns purple (1) and 4.06×10^{-6} M Pu, turns pink (2). (c): 1×10^{-3} – 1×10^{-7} M U contacted with Br-PADAP: PAN in a 2:1 ratio at 1×10^{-5} M U. (d): 1×10^{-4} M Br-PADAP: PAN in a 2:1 ratio at 1×10^{-4} M U traced drinking water (tap) turns purple. The visible color range for concentrations of ppm to ppb uranium indicates both a large detection potential range and a color enhancement using the Br-PADAP: PAN mixture over Br-PADAP alone. No counter anion was needed for stabilization of the U: Br-PADAP: PAN complex.



(a)



(b)



(c)



(d)

Figure 3. (a): Rapid mini column extraction system using prepackaged TEVA/U-TEVA resin cartridges with multiple chamber resin separation columns. Multiple chambers could be combined for compact and fast sample preparation and/or separation and indicator detection. (b): Br-PADAP: PAN (2:1 ratio) sprayed on the surface of a towel gives a purple color indicative of U at $1 \times 10^{-5} \text{M}$. (c): Wipe impregnated with the Br-PADAP: PAN 2:1 ratio solution was contacted by wiping a surface with $1 \times 10^{-5} - 1 \times 10^{-7} \text{M}$ U. The multiple visible colors on the contacted wipe indicates a range of U concentration detection. (d): Clean, uncontacted, CoDeAc wipe.

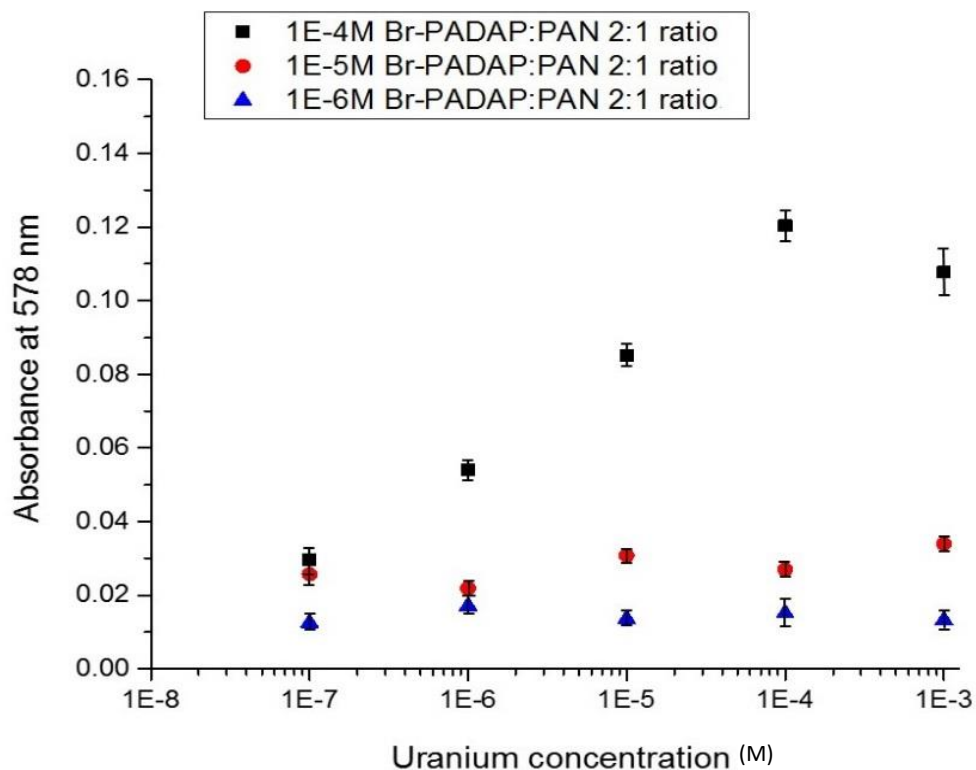


Figure 4. All Br-PADAP and PAN concentrations for this experiment were $1\text{E-}5\text{M}$. This was found to be the optimal concentration for this indicator. Ultraviolet visible spectra of U using a combination of Br-PADAP: PAN in a 2:1 ratio indicated a significantly higher absorbance over Br-PADA and NaF alone. The visual color using this combination in a 2:1 ratio Br-PADAP: PAN was significantly enhanced with Br-PADA alone, which gave an absorbance no higher than 0.005nm in previous experimental work.

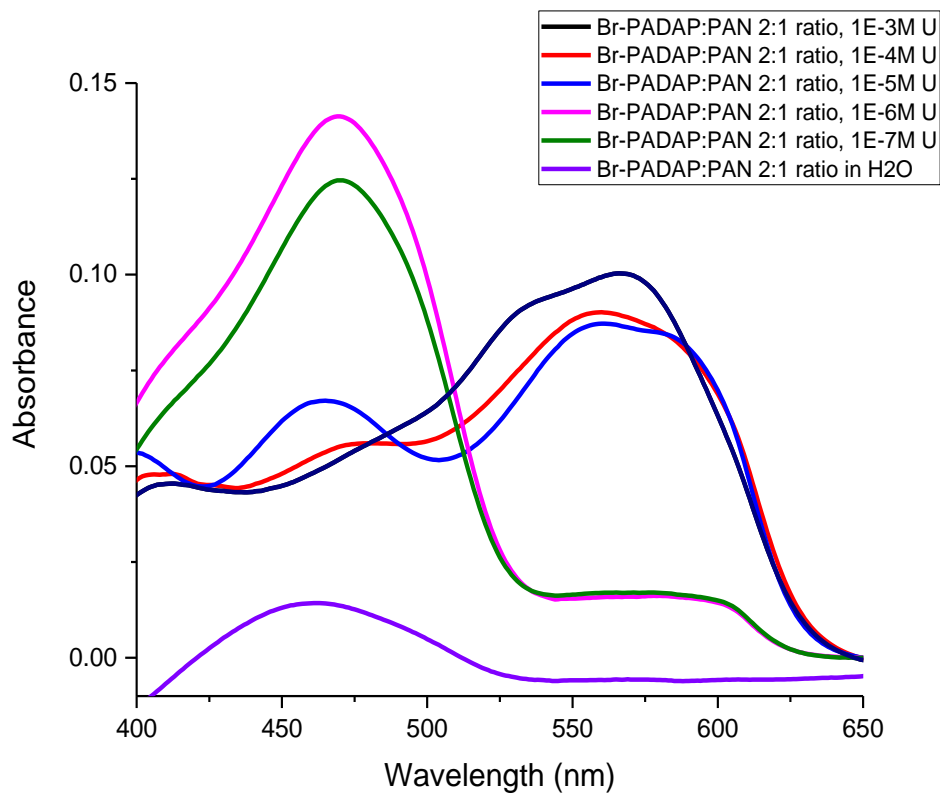


Figure 5. The CoDeAc solution of Br-PADAP: PAN in a 2:1 ratio at 1E-5M contacted with varied concentrations of U from 1E-3M – 1E-7M. A background sample of Br-PADAP: PAN in D.I. H₂O is also shown.

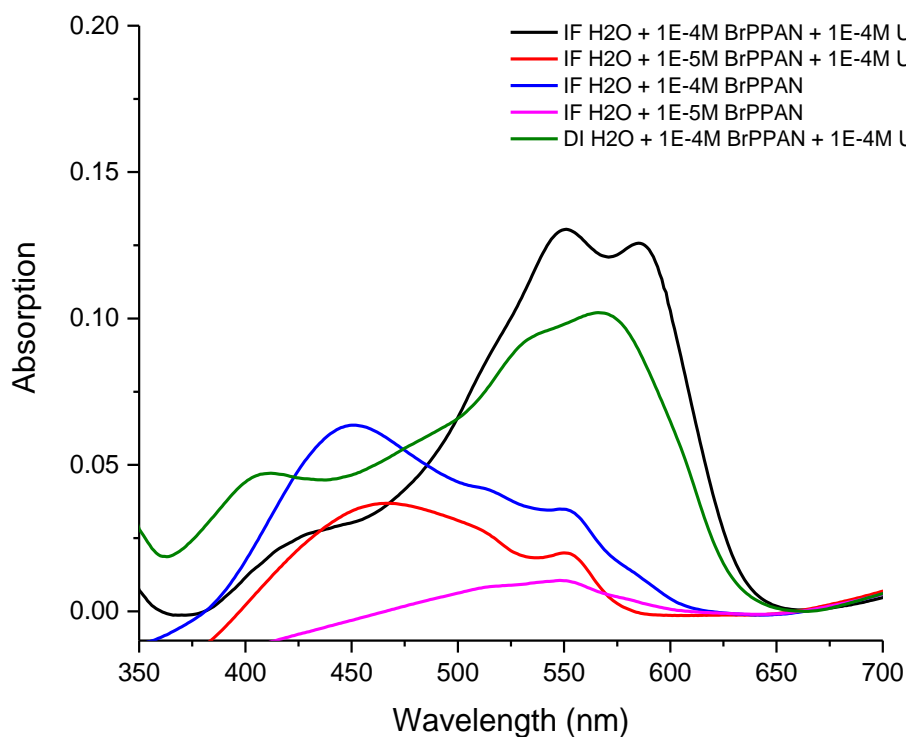


Figure 6. Idaho Falls (IF) drinking water test for iron interference with the CoDeAc solution in the presence of uranium (U). In the 2:1 ratio of Br-PADAP: PAN at 1E-4M for both compounds, U preferentially complexed with CoDeAc over iron in drinking water and gave a vivid color change to dark violet. Without U present, the color of the drinking water combined with the CoDeAc solution is pale peach indicative of the iron complexation.

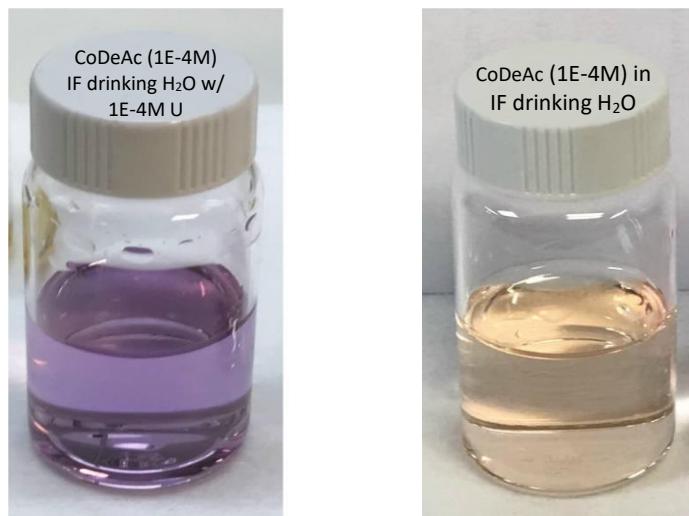


Figure 7. Untraced IF drinking water with CoDeAc solution (1E-4M, 2:1 ratio), right side. IF drinking water traced with 1E-4M U (uranyl nitrate in H₂O) and contacted with CoDeAc solution. IF drinking water is 0.3mg/L Fe and <15 pCi/L U. The slight color change in the untraced water sample is due to Fe complexation.